Biomarker and carbon isotope variation in coal and fossil wood of Central Europe through the Cenozoic

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ABSTRACT

Carbon isotope analyses of terrigenous organic matter are often used to reconstruct changes in the isotopic composition of upper ocean and atmospheric carbon reservoirs. Carbon isotope values from tree-rings, fossil wood, and coal matrices have been related to climatic change (e.g. temperature, humidity) via water-use efficiency of land plants. In this study, we report on carbon isotope analyses on low-rank coal deposits of the Alpine Realm and Middle German Lignite District covering the Early Eocene to Pliocene time interval.

Fossil wood and extracted wood cellulose from gymnosperms and angiosperms, respectively, are used for paleoenvironmental reconstructions. The trend in $\delta^{13}C$ is parallel to the carbon isotope record obtained from benthic foraminifera, because both data sets sample a common reservoir in the atmosphere.

The evaluation of the magnitudes of $\delta^{13}C$ variations of coal caused by environmental change, requires the correction of the $\delta^{13}C$ data due to the effects of different contents of lipids in the organic matter, differences in biogeochemical carbon cycling, varying contributions of gymnosperms versus angiosperms to peat formation, and differences in $\delta^{13}C$ of atmospheric CO_2. The resulting carbon isotope record of coal generally co-varies with the estimated variability in mean annual temperatures during the Tertiary, based on paleobotanical data. Changes in humidity and pCO_2 may be responsible for deviations between the isotopic trend and the paleotemperature curve during the Miocene. The obtained temperature coefficient for $\delta^{13}C$ of C3 plants of about 0.3‰/°C is in agreement with the results of previous studies.

1. Introduction

The carbon isotope record of the Cenozoic is well documented from marine carbonates and organic matter (Savin and Yeh, 1981; Veizer et al., 1999; Zachos et al., 2001). Despite the increasing number of data on the isotopic composition of soil carbonate, teeth and other terrestrial materials (Koch, 1998; Retallack, 2004; Retallack and Sheldon, 2004; Bump et al., 2007), a need remains for regional-scale studies of continental environments. Paleobotanical data have been the major source of information on past climatic changes (e.g. Utescher et al., 2000; Uhl et al., 2007). In the light of recent findings, biomarker and carbon isotope systematics in coal and fossil wood are expected to provide valuable information for the reconstruction of floral assemblages and paleoenvironmental changes during the Cenozoic. Carbon isotope analyses of terrigenous organic matter

have been used to reconstruct changes in the isotopic composition of upper ocean and atmospheric carbon reservoirs (Gröcke et al., 1999; Arens et al., 2000) linked to global burial of organic carbon, mass extinctions, dissociation of gas hydrates, and atmospheric CO_2 levels (Jenkyns and Clayton, 1997; Gröcke et al., 1999; Harris and Little, 1999; Arens et al., 2000; Nguyen Tu et al., 2004). Carbon isotope values of cellulose from tree-rings and fossil wood have also been related to climatic change (e.g. temperature, humidity) via water-use efficiency of land plants (Lipp et al., 1991; Feng and Epstein, 1995; Schleser, 1995; Lücke et al., 1999; Edwards et al., 2000; van Bergen and Poole, 2002; Jahren and Sternberg, 2008).

Based on these results, land plants respond to changes in the upper ocean and atmosphere carbon reservoirs as well as in Earth's climate. $\delta^{13}C$ of C3-plants depend on $\delta^{13}C$ of atmospheric CO_2 and a net fractionation resulting from diffusion and photosynthetic uptake of CO_2. The net fractionation is determined by the balance between the rates of diffusional supply and photosynthetic consumption (Farquhar et al., 1989). According to Murray et al. (1998), the following parameters may affect $\delta^{13}C$ of C3-plants: (i) secular change in atmospheric pressure and/or isotope composition of CO_2, (ii) inter-species

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variations and in response to environmental stress, (iii) biochemical fractionation within the plant, (iv) leaf morphology (conifers are more water conservative and assimilate carbon less efficiently than broad leaf species), (v) temperature and humidity variations through the adjustment of stomatal conductance.

The importance of combining detailed molecular information on wood composition with stable isotope data for paleoenvironmental studies has been outlined by previous studies (van Bergen and Poole, 2002; Poole et al., 2004, 2006). The results of combined petrographical, paleobotanical, organic geochemical and stable isotope studies on European coal deposits with a Cenozoic age indicate how interdisciplinary studies can aid further interpretation of paleoenvironmental changes (Kolcon and Sachsenhofer, 1999; Gruber and Sachsenhofer, 2001; Bechtel et al., 2002a,b, 2003a, 2004). In this study, the results obtained during an extensive research project on Tertiary lignites, resinites, fossil wood, and wood cellulose from central Europe are summarized (Bechtel et al., 2003b, 2005, 2007a,b,c). The biomarker and carbon isotope signatures are used to (i) clarify the parameters determining the carbon isotopic composition of coal and fossil wood;

(ii) establish a carbon isotope record of the Tertiary for terrestrial environments; (iii) provide information about changes in atmospheric carbon cycle and climate during the Tertiary.

2. Geological setting and samples

2.1. Alpine realm

The geology, stratigraphy and depositional environments of low-rank coal seams formed within the Alpine Realm in Austria, Slovenia, Hungary and Bulgaria have been outlined in previous publications (Bechtel et al., 2002a, 2003a,b, 2004, 2005, 2007a,b,c). Middle Eocene to Pliocene deposits have been selected for petrographical and geochemical analyses during these previous studies (Fig. 1).

2.2. Middle German lignite district

Paleogene to early Neogene lignite seams from Eastern Germany have been selected because of the availability of detailed geological,
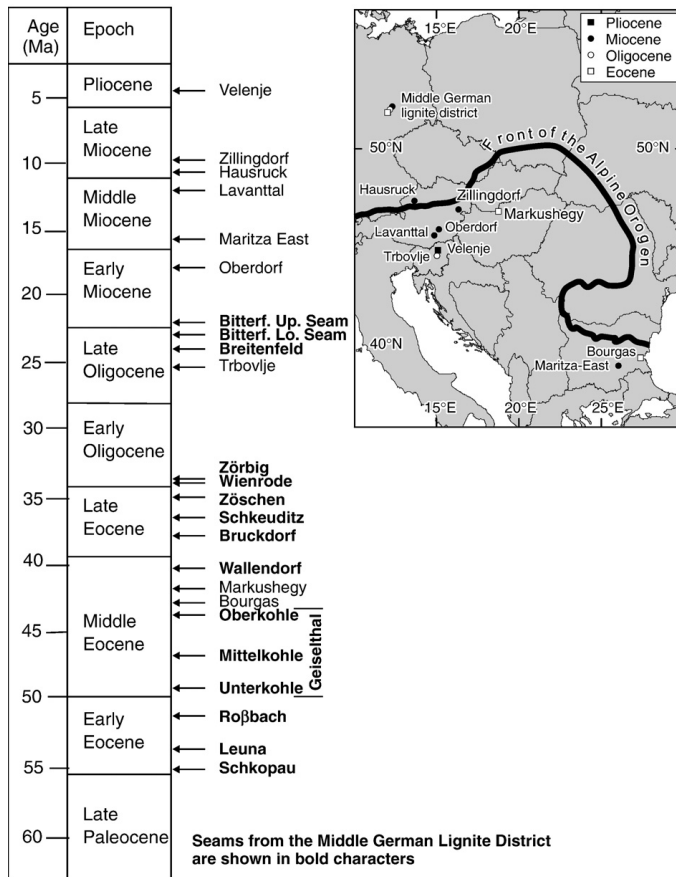

Fig. 1. Chronostratigraphic position of selected lignite seams from the Alpine Realm and the Middle German Lignite District. Insert shows geographic position of coal mines and the front of the Alpine Orogen.

paleobotanical, and stratigraphical data from these deposits (Krutzsch et al., 1992; Blumenstengel et al., 1996; Krutzsch, 2000; Blumenstengel, 2002). The coal seams available for sampling are thought to have been deposited in an estuarine environment at the southern edge of Northwest European Tertiary Sea. The coal formation is related to a climate-regulated transgression–regression process in the Tertiary Sea. Samples were collected from early Eocene to early Miocene lignite seams (Fig. 1). The major results of organic geochemical and stable isotope investigations are compiled in this paper.

3. Analytical methods

From well defined stratigraphic units, coals and coaly shale samples were collected for organic petrological and geochemical analyses. Fossil wood fragments and resinites were also incorporated into the study.

For microscopic investigations, one sample equivalent was crushed to a maximum size of 1-mm. Maceral analysis was performed by a single-scan method (Taylor et al., 1998) with a Leica MPV microscope using reflected white and fluorescent light. At least 300 points were counted. Maceral percentages were used to calculate facies indicators. The Tissue Preservation Index (TPI) and the Gelification Index (GI; Diessel, 1986), modified for low-rank coals (Kalkreuth et al., 1991), are useful facies indicator for lignites (e.g. Bechtel et al., 2002a,b, 2003a) and were calculated according to the following formulas:

$$TPI = \frac{textinite + texto\ ulminite + eu\ ulminite + corpohuminite + fusinite}{attrinite + densinite + macrinite} \qquad (1)$$

$$GI = \frac{text\ ulminite + eu\ ulminite + corpohuminite + densinite + macrinite}{textinite + attrinite + fusinite + inertodetrinite} \qquad (2)$$

For geochemical analyses and carbon isotope determinations, the second sample equivalent was ground and homogenised prior to further treatment. The total carbon and total sulfur contents were determined on a Leco elemental analyser. The organic carbon content (TOC) was measured with the same instrument on samples pre-treated with concentrated hydrochloric acid. For organic geochemical analyses, representative portions of selected samples were extracted for approximately 1 h using dichloromethane in a Dionex ASE 200 accelerated solvent extractor at 75 °C and 5×10^6 Pa. After evaporation of the solvent to 0.5-ml of total solution using a Zymark TurboVap 500 closed cell concentrator, asphaltenes were precipitated from a hexane-dichloromethane solution (80:1) and separated by centrifugation. The fractions of the hexane-soluble organic matter were separated into saturated hydrocarbons, aromatic hydrocarbons, and NSO compounds by medium-pressure liquid chromatography using a Köhnen-Willsch MPLC instrument (Radke et al., 1980).

The saturated and aromatic hydrocarbon fractions were analysed on a gas chromatograph equipped with a 30-m DB-1 fused silica capillary column (i.d. 0.25 mm; 0.25-μm film thickness) and coupled to a Finnigan MAT GCQ ion trap mass spectrometer. The oven temperature was programmed from 70° to 300 °C at a rate of 4 °C min^{-1} followed by an isothermal period of 15 min. Helium was used as carrier gas. The sample was injected splitless with the injector temperature at 275 °C. The mass spectrometer was operated in the EI (electron impact) mode over a scan range from m/z 50 to m/z 650 (0.7 s total scan time). Data were processed with a Finnigan data system. Identification of individual compounds was accomplished based on retention time in the total ion current (TIC) chromatogram and comparison of the mass spectra with published data. Relative percentages and absolute concentrations of different compound groups in the saturated and aromatic hydrocarbon fractions were calculated using peak areas from the gas chromatograms in relation to those of internal standards (deuterated n-tetracosane and 1,1'-binaph-

thyl, respectively). The concentrations were normalised to the total organic carbon content.

Extraction of cellulose from the fossil wood samples was achieved via a acidified sodium chlorite oxidation, modified after Wiesberg (1974). Details of sample preparation and analysis are given by Bechtel et al. (2002b). As a final purification step, treatment with Cuam solution (aq. copper oxide-ammonia) was performed on the cellulose extracted by oxidation.

Carbon isotope measurements of total organic matter, fossil wood and extracted wood cellulose were made on homogenised samples. Portions of each sample (between 1 to 4 mg, cellulose 0.3 mg) were packed in tin capsules and combusted in excess oxygen at 1080 °C using an elemental analyser (Eurovector Instruments and Roboprep, respectively). The resulting CO_2 was analysed online with an Isoprime (Micromass Ltd.) or with an Europa Scientific isotope ratio mass spectrometer interfaced via cryogenic traps. The $^{13}C/^{12}C$ isotope ratio of the CO_2 from a sample was compared with the corresponding ratio of a reference, calibrated against the PDB standard. The reproducibility of the total analytical procedure is in the range of 0.1 to 0.2‰.

4. Results and discussion

The results of the carbon isotope measurements on the total organic matter of the coals from the selected deposits are listed together with some bulk geochemical parameters, liptinite percentages maceral-based facies indicators, and the concentrations of selected organic compound groups and biomarker ratios (Table 1).

4.1. Parameters controlling carbon isotope composition

The comparison of the contents and variability of macerals of the liptinite group within the lignite seams reveals significant differences. The data reflect differences in the contribution of resinous organic matter, leaves, spores/pollens, bark, etc. in relation to humic material to peat formation (Table 1). In several of the investigated lignite seams, negative relationships between the liptinite contents and δ^{13}C values of coal were obtained (Bechtel et al., 2002b, 2005, 2007c; Fig. 2). The results provide evidence, that the carbon isotopic composition of lignite is affected by the content of lipid-rich (e.g. resins, leaves, bark) organic matter. This is supported by the enhanced yields of extractable organic matter (EOM) obtained from liptinite-rich samples.

Degradation of plant tissue is known to affect the carbon isotopic composition of coal (Benner et al., 1987; Schleser et al., 1999; Bechtel et al., 2004, 2007c). The degree of variation of bulk δ^{13}C signatures of fossil land plant material is influenced by the molecular isotope heterogeneity of different moieties (Poole et al., 2004, 2006). The extent of gelification of wood can be examined by microscopy of coal. The maceral-based gelification Index (GI) was found to be positively related to the concentration of hopanoids in several of the investigated lignite seams (Bechtel et al., 2007a; Fig. 3). The most probable biological precursors of the hopane derivatives found in all samples are bacteriohopanepolyols (Ourisson et al., 1979; Rohmer et al., 1992). These compounds have been identified in bacteria and fungi, as well as in some cryptogames (e.g. moss, ferns). The results indicate that gelification of plant tissue is at least partly governed by the activity of bacteria in the peat-forming environment. Degradation by bacteria and/or fungi may cause chances in the isotopic composition of coal due to differences in the decay-resistance of macromolecules (Benner et al., 1987). Negative relationships between the concentration of hopanes and δ^{13}C of lignite were often obtained during our studies (Bechtel et al., 2005, 2007a; Fig. 4). The depletion of lignite in ^{13}C by bacterial activity is most probably caused by the progressive decay of cellulose.

Influences of inter-species variations and of leaf morphology on δ^{13}C of coal were evaluated by the use of paleobotanical data (Krutzsch et al., 1992; Blumenstengel et al., 1996; Bruch, 1998; Haas et al., 1998;

Table 1
Ranges of liptinite contents, gelification index (GI), tissue preservation index (TPI), and concentration of hopanoids, as well as concentration ratios of diterpenoids to the sum of diterpenoid plus angiosperm-derived triterpenoid hydrocarbons, average, minimum, and maximum $\delta^{13}C$ values of coal samples

Locality seams	Age (Ma)	Liptinite (vol.%, mmf)	GI	TPI	Hopanoids (µg/g TOC)	Di-/(Di- + Tri-terpenoids)	$\delta^{13}C$ Coal (‰, PDB) Mean	$\delta^{13}C$ Coal (‰, PDB) Min	$\delta^{13}C$ Coal (‰, PDB) Max
Velenje	4.5	4–13	0.4–2.8	0.5–4.3	19–41	0.79–0.99	−26.2	−27.4	−25.3
Zillingdorf	9.5	2–11	5.0–44.4	0.2–9.7	31–82	0.46–0.96	−25.7	−27.2	−24.6
Hausruck	10.5	10–47	0.5–17.9	0.5–4.0	31–388	0.10–0.77	−25.9	−27.4	−24.9
Lavanttal	11.8	1–22	3.8–27.7	0.4–8.4	67–164	0.34–0.93	−25.3	−26.7	−24.2
Maritza-East	15.5	12–26	0.3–1.5	0.2–1.2	74–166	0.85–0.98	−24.6	−25.2	−23.9
Oberdorf	17.5	5–34	0.7–6.0	0.2–7.2	37–275	0.74–0.94	−24.7	−26.0	−23.8
Bitterf. US	21.7	4–46	1.4–78.3	0.0–1.7	110–235	0.05–0.31	−25.0	−25.3	−24.8
Bitterf. LS	22.5	5–38	0.5–59.6	0.1–4.2	73–216	0.07–0.58	−25.3	−25.8	−24.4
Breitenfeld	23.7	0–34	1.4–11.8	0.1–1.0	63–263	0.11–0.19	−25.8	−26.5	−25.6
Trbovlje	25.0	0–51	0.6–49.0	0.0–15.0	22–135	0.48–0.98	−25.6	−26.8	−24.0
Zörbig	33.4	1–16	5.4–68.7	0.0–0.2	98–147	0.15–0.24	−26.3	−26.8	−25.7
Wienrode	33.7	21–31	193.9	0.0–0.1	188–372	0.10–0.13	−26.7	−26.8	−26.5
Zöschen	34.7	4–30		0.0–0.2	63–150	0.08–0.23	−26.4	−26.6	−25.9
Schkeuditz	36.2	7–15	0.1–4.2	0.0–0.1	53–108	0.04–0.07	−26.0	−26.1	−25.7
Bruckdorf	37.5	0–40	0.6–70.2	0.0–0.3	61–198	0.01–0.07	−25.8	−26.6	−25.5
Wallendorf	40.0	9–14	8.4	0.0–0.6	97–125	0.03–0.06	−25.9	−26.2	−25.5
Markushegy	41.5	4–42	0.2–32.3	0.1–1.5	57–324	0.04–0.14	−25.6	−26.3	−24.7
Bourgas	42.5	2–12		0.0–0.6	87–215	0.05–0.45	−25.8	−26.4	−24.9
Geiseltal Oberkohle	43.5	8–28		0.0–0.3	82–498	0.02–0.04	−25.5	−25.7	−25.3
Geiseltal Mittelkohle	46.5	6–22	9.8	0.0–0.2	190–461	0.02–0.05	−25.8	−26.2	−25.2
Geiseltal Unterkohle	49.0	8–77	5.6–35.2	0.0–0.2	131–260	0.01–0.06	−25.7	−26.0	−25.2
Rossbach	51.0	3–32	7.5–79.8	0.0–0.1	109–355	0.02–0.07	−25.3	−26.2	−24.0
Leuna	53.5	4–23	3.0–239.3	0.0–0.5	91–185	0.03–0.17	−25.2	−25.9	−24.4
Schkopau	55.0	1–33	0.7–61.6	0.0–0.7	99–202	0.01–0.08	−25.2	−26.0	−24.5

GI = Gelification Index, TPI = Tissue Preservation Index, TOC = Total organic carbon, Diterpenoids = Sum of diterpenoid hydrocarbon concentrations, Triterpenoids = Sum of concentrations of angiosperm-derived triterpenoid hydrocarbons.
Data of lignite seams from the Alpine Realm are taken from Bechtel et al. (2002a,b, 2003a,b, 2004, 2005, 2007a,b,c).

Kolcon and Sachsenhofer, 1999) and/or by biomarker composition of the lignite samples (Bechtel et al., 2002a, 2003a,b, 2004, 2005, 2007a, b,c). The results indicate that, at least, differences in the contribution of gymnosperms (conifers) versus angiosperms to peat formation can be recognized from biomarker composition. The hydrocarbons of lignites derived from coniferous wood are dominated by sesquiterpenoids and diterpenoids. In contrast, angiosperm-derived coal shows high contents of triterpenoids of the oleanane, ursane, or lupane structural types. The concentration of diterpenoid biomarkers (including abietane-, pimarane-, isopimarane-, beyerane-, kaurane-, and phyllocladane-type hydrocarbons) relative to the sum of diterpenoid hydrocarbons plus angiosperm-derived triterpenoid hydrocarbons (i.e. oleanane, ursane, lupane-derivatives) have been used as proxies for the contribution of gymnosperms versus angiosperms to peat formation.

The results are in general agreement with reconstructions based on paleobotanical information. The contents of gymnosperm-specific biomarkers relative to the summarized contents of land plant-derived terpenoid hydrocarbons were found to correlate with the percentages of coniferales pollen obtained from the sample set of the Oberdorf lignite seam (Fig. 5; Kolcon and Sachsenhofer, 1999; Bechtel et al., 2002a). However, a higher percentage of conifers to peat formation is indicated by the biomarker ratios (Fig. 5). This difference may be explained by the fact that palynomorphs represent the vegetation in the area of the swamp, whereas biomarker ratios reflect the plant community that built up the peat. The influence of changing contributions of gymnosperm and angiosperms on $\delta^{13}C$ of coal is indicated by positive relationships obtained from several deposits (Fig. 6). This effect is caused by on average 2.5‰ isotopically heavier $\delta^{13}C$ values of gymnosperms in comparison to angiosperms due to differences in leaf morphology and carbon assimilation efficiency (Murray et al., 1998).
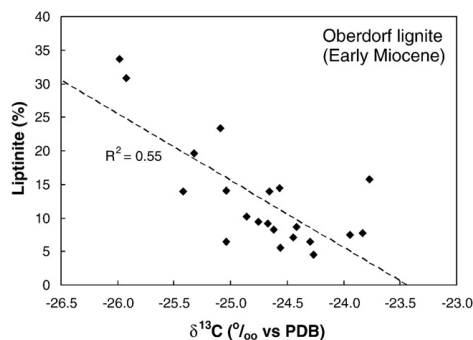

Fig. 2. Relationship between the contents of macerals of the liptinite group and $\delta^{13}C$ of coal within the Early Miocene Oberdorf lignite seam (adopted from Bechtel et al., 2002b).
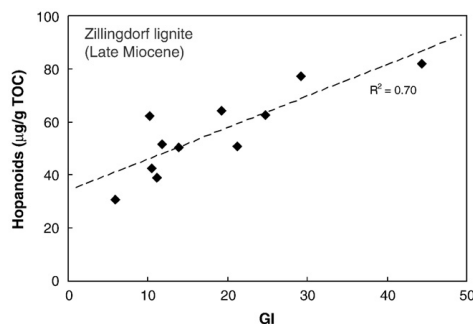

Fig. 3. Cross-correlation between the gelification index (GI) and hopanoid contents of lignite from the Late Miocene Zillingdorf deposit (adopted from Bechtel et al., 2007a).
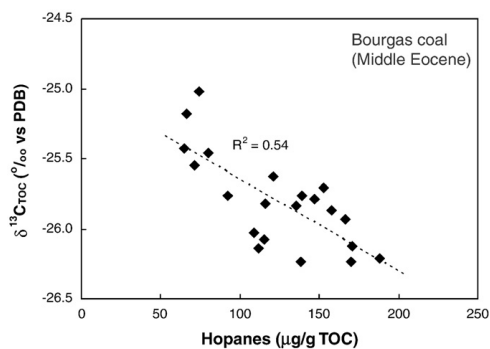
Fig. 4. Relationship between the $\delta^{13}C$ values of the coal and the concentration of hopanes within the Middle Eocene Bourgas coal (adopted from Bechtel et al., 2005).

Fig. 6. Correlation diagram between the $\delta^{13}C$ values of the coal and the concentration ratios of diterpenoids versus the sum of di- plus angiosperm-derived triterpenoid hydrocarbons within the Bourgas coal deposit (adopted from Bechtel et al., 2005).

4.2. Terrestrial carbon isotope record

The biomarker and isotopic results from different coal deposits are summarized in Fig. 7. The average $\delta^{13}C$ of coal as well as minimum and maximum values of each deposit are shown together with the results obtained on fossil wood from gymnosperms and angiosperms, respectively (Table 1; Fig. 7). Based on the di- versus di- plus angiosperm-derived triterpenoids ratio (Table 1), a pronounced shift from an angiosperm-dominated vegetation during Eocene up to the Early Oligocene towards gymnosperm-derived coal in the Neogene is indicated (Fig. 7). Generally, lignite samples predominantly derived from coniferous wood are characterized by higher tissue preservation index (TPI) values (Table 1). The results are consistent with the higher decay-resistance of wood from gymnosperms as compared to angiosperms (Hatcher and Clifford, 1997). The difference in peat-forming vegetation is further reflected by the $\delta^{13}C$ values. The data indicate an influence of the floral assemblage on the isotopic composition of terrestrial organic carbon.

To eliminate this effect together with the other influencing parameters on $\delta^{13}C$ of coal (see Section 4.1), the carbon isotope composition of fossil wood may be used. Carbon isotope ratios of fossil wood fragments and extracted cellulose are compiled from the results obtained during previous studies (Bechtel et al., 2002b, 2003a,b,
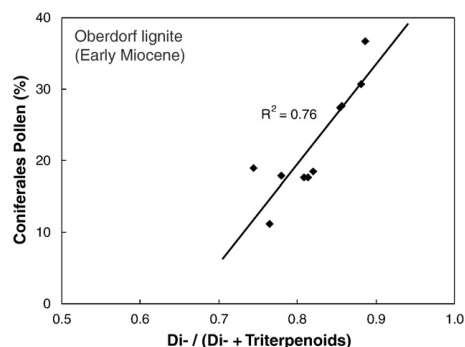
2004, 2007a,b). However, these data are limited to lignite seams where fossil wood of good preservation could be found (Fig. 7). Furthermore, cellulose-decay is known to affect $\delta^{13}C$ of wood (Benner et al., 1987; Lücke et al., 1999). In contrast to fossil wood, $\delta^{13}C$ of extracted wood cellulose is only negligibly influenced by decomposition (Schleser et al., 1999; Bechtel et al., 2003a). Therefore, $\delta^{13}C$ of wood cellulose from either gymnosperms or angiosperms could be used to identify possible relations to the isotopic variability of carbon reservoirs and paleoclimate. In Fig. 7, available mean data from gymnosperms are interpolated. Generally, a reasonably good co-variation with $\delta^{13}C$ values obtained from benthic taxa is obtained, indicating the effect of changing isotopic composition of carbon reservoirs. Resinites provide consistent records in $\delta^{13}C$ (Fig. 7). However, coal data must be used in order to increase the resolution of the carbon isotope record. Parallel trends with $\delta^{13}C$ of benthic taxa (Zachos et al., 2001) as well as mean annual temperature estimates based on paleobotanical data (Eissmann, 1994) are evidenced by the data set (Fig. 7).

4.3. Carbon cycle and climate

In order to reconstruct the magnitudes of $\delta^{13}C$ variations in low-rank coals caused by environmental change during the Tertiary (e.g. CO_2 concentration of the atmosphere, temperature, humidity), the possible effects of differences in land-plant detritus, supplied to the mires, and their resistance against microbial decomposition must be considered. Furthermore, the carbon isotopic variability due to varying contributions of gymnosperms versus angiosperms to coal formation should be taken into account.

The correction of the average $\delta^{13}C$ of lignite from each deposit towards lipid-poor plant tissue (Table 2) was achieved by extrapolating existing relationships towards low liptinite contents or by excluding the data of liptinite-rich coal. The same procedure was applied for the correction towards low hopanoid contents or gelification index (Table 2). In the case of absent links between liptinite and/or hopanoid contents and $\delta^{13}C$, the average $\delta^{13}C$ of coal remained uncorrected (no data in the respective column of Table 2). The data were further corrected by adjusting the $\delta^{13}C$ values towards gymnosperm-dominated vegetation using the respective relationships between the di-/(di- plus triterpenoid) ratios and $\delta^{13}C$ of coal (Table 2). For most of the angiosperm-rich Paleogene coals, the correction was achieved by using the average difference of 2.5‰ between gymnosperm and angiosperm wood. Samples with contributions from gymnosperms

Fig. 5. Cross-correlation of the di- to di- plus angiosperm-derived triterpenoids ratios versus the relative proportions of coniferales pollen of the coal from the Oberdorf lignite seam (adopted from Bechtel et al., 2002a).
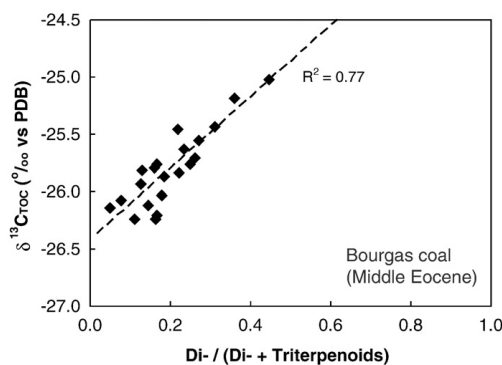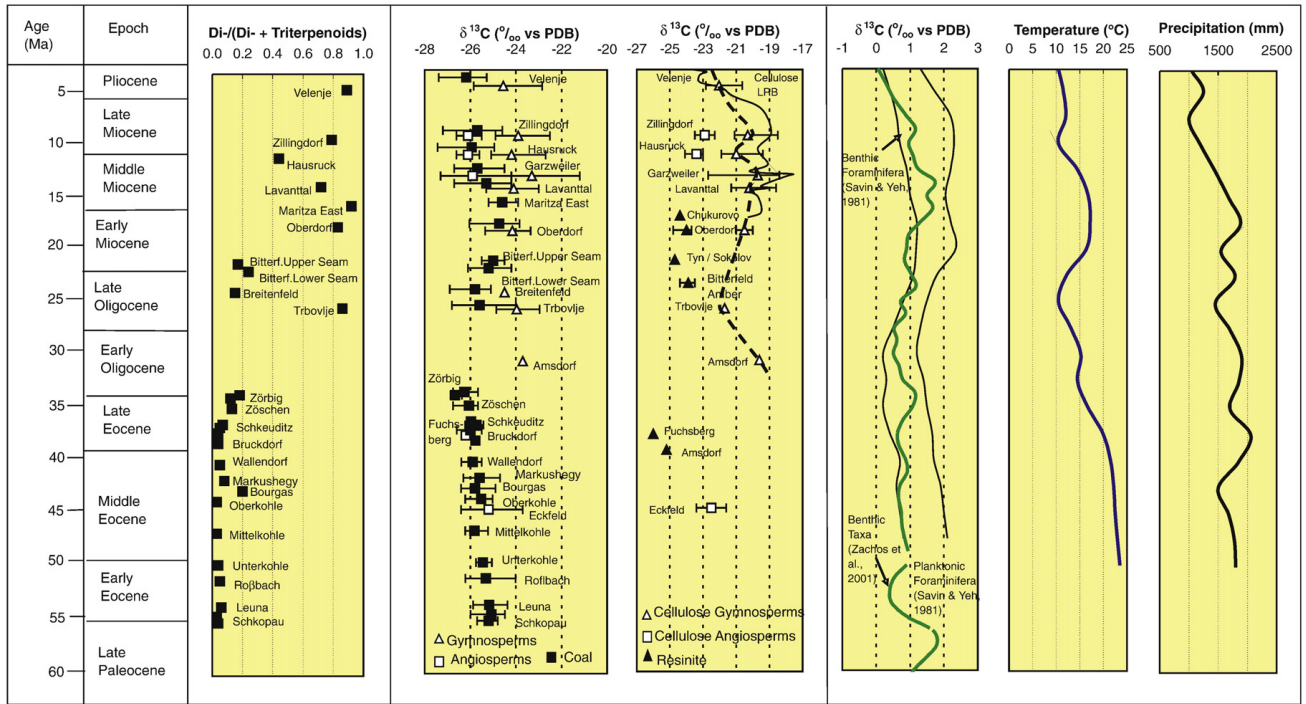
Fig. 7. Variation of the di- to di- plus angiosperm-derived triterpenoids ratios, the δ^{13}C of coal (average, minimum, and maximum values), δ^{13}C of fossil wood, extracted wood cellulose (data from the Lower Rhine Basin according to Jordan, 1995), and resinites, carbon isotope records from benthic and planktonic foraminifera, as well as estimates about the variability of mean annual temperatures and precipitation in central Europe during the Tertiary based on paleobotanical data (Krutzsch et al., 1992; Eissmann, 1994; Blumenstengel et al., 1996; Bruch, 1998; Haas et al., 1998; Kolcon and Sachsenhofer, 1999). Data of fossil wood and wood cellulose from the Alpine Realm are compiled from Bechtel et al. (2002b, 2003a,b, 2004, 2007a,b).

Table 2
Average $\delta^{13}C$ values of coal corrected for liptinite contents, hopanoid contents and GI, respectively, and $\delta^{13}C$ corrected towards gymnosperm-dominated vegetation, and for the C-isotope variability of atmospheric CO_2, based on $\delta^{13}C$ records from benthic foraminifera (Zachos et al., 2001)

Locality seams	Age (Ma)	$\delta^{13}C$ Coal (‰, PDB) corrected for Liptinite	$\delta^{13}C$ Coal (‰, PDB) corrected for Hopanoids or GI	$\delta^{13}C$ Coal (‰, PDB) corrected for Gymn/ (Angio+Gymn)	$\delta^{13}C$ Coal (‰, PDB) corrected for $\delta^{13}C$ of CO_2
Velenje	4.5		−25.8	−25.6	−25.6
Zillingdorf	9.5		−25.2	−24.9	−25.9
Hausruck	10.5	−25.5	−25.1	−24.3	−25.1
Lavanttal	11.8		−24.5	−24.1	−25.6
Maritza-East	15.5	−24.4		−24.4	−25.7
Oberdorf	17.5	−24.6	−24.8	−23.8	−24.9
Bitterf. US	21.7	−24.9		−23.6	−24.2
Bitterf. LS	22.5		24.9	−24.1	−24.9
Breitenfeld	23.7		−25.0	−24.4	−25.4
Trbovlje	25.0	−25.4		−25.2	−25.7
Zörbig	33.4	−26.5		−23.5	−24.3
Wienrode	33.7		−26.1	−23.8	−24.8
Zöschen	34.7		−26.0	−23.5	−24.4
Schkeuditz	36.2		−25.8	−23.3	−23.9
Bruckdorf	37.5	−25.8		−23.3	−23.7
Wallendorf	40.0	−25.5		−23.0	−23.7
Markushegy	41.5	−25.4		−23.2	−23.9
Bourgas	42.5	−25.4		−23.5	−24.0
Geiseltal Oberkohle	43.5		−25.3	−23.1	−23.6
Geiseltal Mittelkohle	46.5		−25.7	−23.2	−23.8
Geiseltal Unterkohle	49.0	−25.4		−22.6	−23.2
Rossbach	51.0	−25.2		−22.7	−23.1
Leuna	53.5	−25.1	−25.0	−22.6	−22.9
Schkopau	55.0	−25.0	−24.7	−22.3	−23.2

Gymno = Gymnosperms, Angio = Angiosperms.
The average $\delta^{13}C$ of coal remained uncorrected (no data in the respective column) in the case of missing relationship between the respective parameter and $\delta^{13}C$.

and angiosperms are corrected by multiplication of this difference in $\delta^{13}C$ with the di- versus di- plus triterpenoid ratio. The applied procedures for the correction of $\delta^{13}C$ data resulted in additional uncertainties in the range of 0.3 to 0.5‰ (e.g. 1σ error limits of linear regression lines).

The trend in corrected $\delta^{13}C$ generally co-varies with estimates about the variability in mean annual temperature during the Tertiary, based on paleobotanical data from central Europe (Krutzsch et al., 1992; Eissmann, 1994; Blumenstengel et al., 1996; Bruch, 1998; Haas et al., 1998; Kolcon and Sachsenhofer, 1999). Information about changes in paleoclimate was derived from compilations of these paleobotanical data using the coexistence approach, a method that employs climatic requirements of the nearest living relatives of the fossil floras (Eissmann, 1994; Fig. 8). Deviations may be caused by the low time resolution of the available data from lignite seams. Furthermore, an additional correction is needed to eliminate the effect of changes in $\delta^{13}C$ of atmospheric CO_2 on the $\delta^{13}C$ of C3 plants (Farquhar et al., 1980). The high-resolution record of $\delta^{13}C$ of benthic taxa during the Cenozoic (Zachos et al., 2001) reflects the variability in $\delta^{13}C$ of atmospheric CO_2. The applied correction is based on the fact that the relative differences in the carbon isotope composition of CO_2 during the Tertiary result in similar differences in $\delta^{13}C$ of C3 plants.

The resulting carbon isotope trend (bold line in Fig. 8; Table 2) is suggested to reflect the response of C3 plants due to climatic change (e.g. CO_2 concentration of the atmosphere, temperature, humidity). Despite major discrepancies in the proxy data used for the reconstruction of atmospheric CO_2 level variations in the Tertiary, a generally higher CO_2 concentration is assumed during Eocene times as compared with the Miocene (Pagani et al., 1999; Pearson and Palmer, 2000; Royer et al., 2001). The stomatal frequency response to changing CO_2 levels, based on cuticle remains of oak leaves from late Miocene to early Pleistocene sediments of the Lower Rhine Embayment (Germany), indicated fluctuations between 280 and 370 ppmv with enhanced values during warm-temperate to subtropical climatic conditions (Kürschner et al., 1996). An enhanced atmospheric CO_2 level would result in additional fractionation of C3 plants and, therefore, lower $\delta^{13}C$ values during Eocene as compared to the Miocene (Feng and Epstein, 1995; Kürschner, 1996). However, the results on oak leaves grown under different CO_2 levels argue for an insignificant response of $\delta^{13}C$ of land plants on long-term pCO_2 variations (Nguyen Tu et al., 2004). Differences in mean annual precipitation and temperature are, therefore, implied as the responsible factors for the reconstructed record in $\delta^{13}C$ of land plants.

The corrected trend in $\delta^{13}C$ is more or less parallel to the temperature curve, with the exception of deviations in the middle and lower Miocene (Fig. 8). The data are in general agreement with previous results indicating a temperature coefficient of about 0.3‰/°C (Lipp et al., 1991; Schleser, 1995; Lücke et al., 1999). Deviations during the Miocene may be caused by the influences of humidity variations on $\delta^{13}C$ of land plants (Fig. 8). Based on previous studies, the sensitivity of $\delta^{13}C$ to relative humidity has been inferred as −0.17‰/% (Edwards et al., 2000).

5. Summary and conclusions

Cross-correlations of petrographical, organic geochemical and stable isotope data indicate, that the $\delta^{13}C$ values of low-rank coal deposits of early Eocene to Pliocene age of central Europe are influenced by differences in the composition of land plant tissue and their resistance against microbial degradation, biogeochemical carbon cycling, as well as by varying contributions of gymnosperms versus angiosperms to peat formation. Based on biomarker ratios, angiosperms predominated in the peat-forming vegetation of central Europe during Eocene up to the early Oligocene, whereas a gymnosperm-dominated vegetation is indicated during the Neogene.

In order to evaluate the magnitudes of $\delta^{13}C$ variations caused by environmental changes during the Tertiary, average carbon isotope data of coal with low contents of liptinite macerals and low hopanoid concentrations are compared. The $\delta^{13}C$ values of the respective gymnosperm-dominated vegetation are reconstructed from the terpenoid biomarker composition and their relationships to the carbon isotopic composition of the coal seams. The $\delta^{13}C$ data of the coal deposits are further corrected because of differences in $\delta^{13}C$ of atmospheric CO_2 during the Tertiary, reconstructed from the $\delta^{13}C$ values of benthic foraminifera.

Differences in atmospheric CO_2 level as well as variations in mean annual precipitation of central Europe, are insufficient to explain the obtained differences in $\delta^{13}C$. Parallel trends with estimates about the variability in mean annual temperatures based on paleobotanical data are obtained. The corrected $\delta^{13}C$ values of coal are therefore considered as proxies of climatic changes (i.e. temperature, humidity).

The present study suggests that the observed patterns were primarily produced by variations of the isotope ratios of oceanic and atmospheric carbon reservoirs, and additionally modified by climatic changes due to their influence on plant physiology. Thus, the terrestrial carbon isotope record indicates changing $\delta^{13}C$ values of atmospheric CO_2 associated with atmospheric pCO_2 and paleoclimate. Carbon isotope studies on lignite, fossil wood of known taxa and on their cellulose provide a powerful tool in reconstructing the isotopic record of land plants and its implication for environmental changes during the Earth's history. Further studies are needed to fully exploit the potential of carbon isotope data of coal for paleoenvironmental reconstructions.
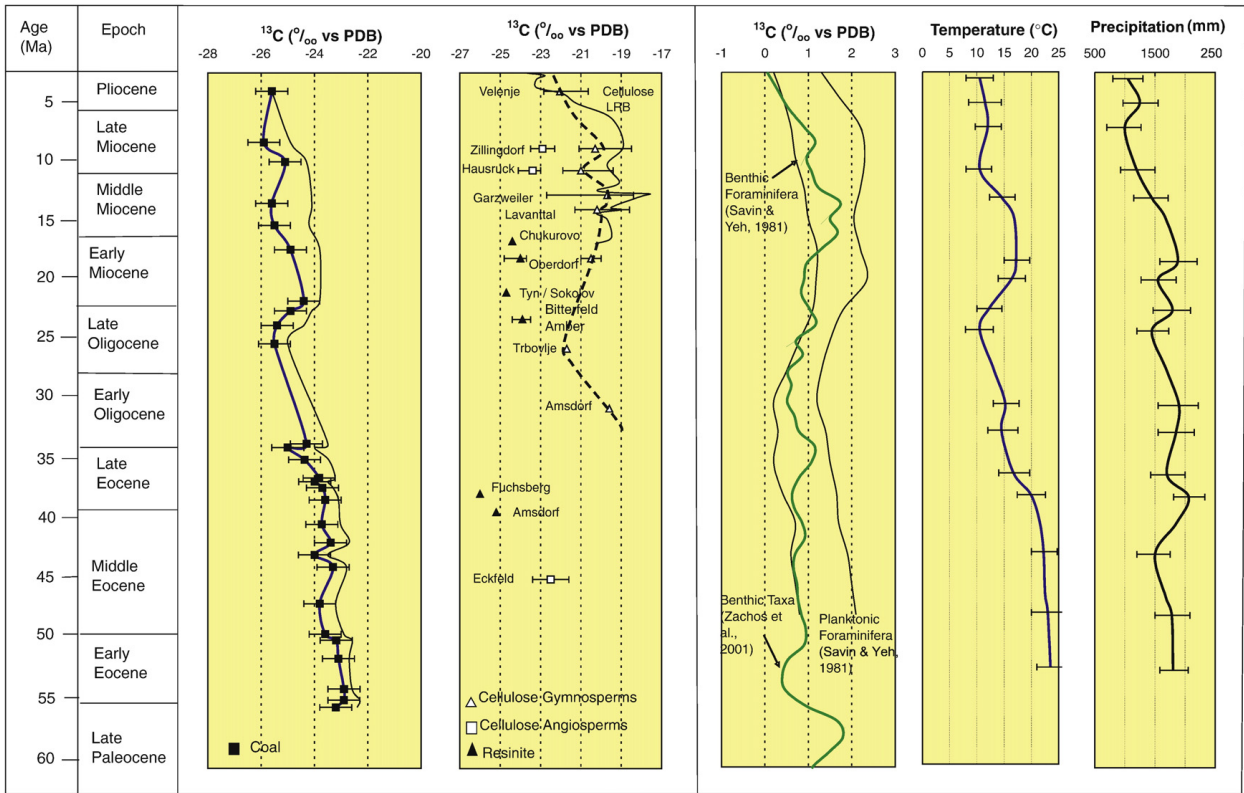
Fig. 8. Variation of δ^{13}C of terrestrial organic matter corrected for the effect of liptinite and hopanoid contents, gelification index and varying contributions of angiosperms to peat formation on δ^{13}C of coal (thin solid line), as well as after additional correction for the effect of changing δ^{13}C values of atmospheric CO_2 on δ^{13}C of C3 plants (bold line), δ^{13}C of fossil wood, extracted wood cellulose (data from the Lower Rhine Basin according to Jordan, 1995), and resinites, carbon isotope records from benthic and planktonic foraminifera, as well as estimates about the variability of mean annual temperatures and precipitation in central Europe during the Tertiary based on compilations of paleobotanical data (Krutzsch et al., 1992; Eissmann, 1994; Blumenstengel et al., 1996; Bruch, 1998; Haas et al., 1998; Kolcon and Sachsenhofer, 1999).

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